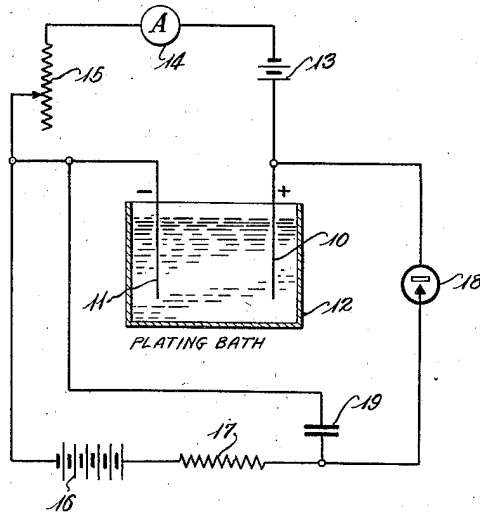


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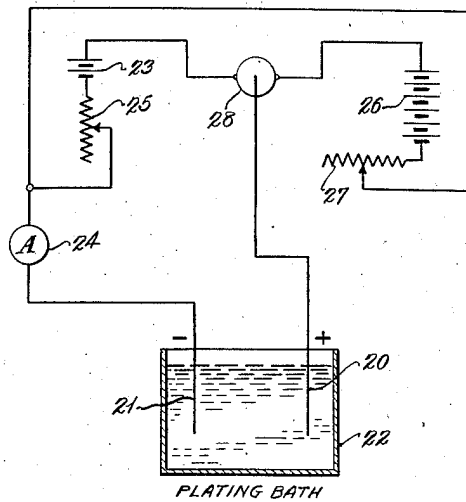
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ELECTROLYTIC METHOD FOR THE PRODUCTION  
OF POROUS, CATALYTIC METAL  
Filed June 2, 1944

2,453,668

*Fig. 1.*



*Fig. 2.*



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# UNITED STATES PATENT OFFICE

2,453,668

## ELECTROLYTIC METHOD FOR THE PRODUCTION OF POROUS, CATALYTIC METAL

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Application June 2, 1944, Serial No. 538,388

2 Claims. (Cl. 204-49)

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This invention relates to a porous adherent metallic body produced by electroplating and to the process of electroplating by which such body is produced.

Elementary metals function as catalysts for a number of chemical reactions, among the more important of which are hydrogenation of olefins and the like. Numerous proposals have been made for preparing porous metals for catalytic uses, such as leaching of sodium alloys, deposition of nitrates on carriers followed by calcining to the oxide and reduction, etc. We have now found that porous metal bodies of high structural strength and great catalytic activity may be produced by a process of electrolytic deposition described hereinafter.

The electrolytic deposition of metals to form smooth, adherent coatings requires the control of a number of variables which are as follows:

1. Current density.
2. Agitation of plating solution.
3. Concentration of plating solution.
4. Temperature of plating solution.

Excessive current densities, high temperatures and/or concentrated solutions result in spongy, porous platings which peel readily and may be rubbed off very easily. Failure to agitate the electrolytic solution, or a too low rate of agitation, permits the accumulation of bubbles of hydrogen gas on the cathode and thus, there is formed a pitted and non-adherent plating. Low current densities with very dilute solutions result in porous platings. Such platings are known in the art, chiefly because they are to be avoided. Obviously, they have not attained commercial use.

Electrolytic platings of a porous nature produced under the above conditions yield efficient metallic catalysts. Platinum black is such a catalyst, but its use as a catalyst has been limited to academic interests because of its non-adherent quality. This disadvantage explains why porous metallic platings have not found practical use as catalysts.

This invention has for its purpose a method of preparing metallic catalysts which involves alternatively plating metals by electrolytic means at conditions which produce a porous plating followed by a smooth adherent plating, and so on, to build up a multiplicity of porous and smooth layers. The thickness of each layer may be varied throughout wide limits, however, a thickness of a 100 to 1000 metallic atoms for each layer appears to be satisfactory from the practical standpoint.

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In this process, control of pH is much less important than is the case when shiny deposits are desired. In all cases, it was found that pH may vary widely without material effect on the nature of the deposit according to the present invention. As a general rule, pH may vary between about 3 and 7.5 in practice of this invention.

The simplest method of practicing this invention consists of periodically varying the current density by a suitable timing device. Thus the electrolytic plating is conducted for a short period of time, as for example five seconds at the current density which produces a smooth adherent coating, followed by plating at a high current density for another short interval of time, and so on. The intervals of time at which the two types of plating are conducted may be equal or they may be varied considerably.

Another method involves periodically agitating or circulating the electrolytic solution to build up successive porous and non-porous layers. Still another procedure consists of moving the cathode periodically from the electrolytic bath maintained at room temperature to another bath held at an elevated temperature. Or, the two electrolytic baths may be composed of solutions of different concentrations; the one bath containing a solution which gives the smooth plating, while the other contains a concentrated solution which will result in a porous plating.

Other methods of producing the catalysts of this invention are illustrated in the specific examples. They involve plating from an electrolytic bath at a current density which produces a smooth coating and simultaneously impressing sudden surges of exceedingly high voltages at short intervals of time. Thus, lower current densities are required to produce porous, adherent platings than are necessary when low voltages are employed. The presence of suspensions in the electrolytic bath such as, for example, silica gel or precipitate at low current densities results in spongy, adherent platings. Metals which are non-porous and not-catalytic may be converted into porous catalysts by deplating and replating in a suitable electrolytic bath. This latter method offers a means of regenerating the spent catalysts of this invention.

Apparatus for preparing the catalytic porous metals of this invention is shown in the drawings annexed hereto, wherein:

Figure 1 is a diagrammatic illustration of apparatus for plating at regularly varied current densities; and

Figure 2 is a diagram of apparatus functioning

in similar manner but having a different type of control.

Referring particularly to Figure 1, an anode 10 and a cathode 11 are immersed in an electrolytic plating cell 12. A primary battery 13, or other source of D. C. potential, is connected to the anode and cathode through an ammeter 14 and a variable resistance 15. The potential applied across the cell 12 between anode 10 and cathode 11 is adjusted and correlated to composition of the bath, temperature, etc., to plate the desired metal from the bath on the cathode as a smooth adherent layer. A secondary battery 16 is also connected across the plating bath in a circuit which includes resistance 17 and discharge tube 18. A condenser 19 is connected in parallel with the battery 16 and resistance 17. The condenser is charged at rate depending on the electromotive force applied by the battery 16 or its equivalent, the resistance of element 17 and the capacity of the condenser until the potential across the condenser reaches the breakdown potential of tube 18. A surge of current will then flow, discharging the condenser until the potential across the latter drops to the cutoff potential of the tube, whereupon flow in the secondary circuit will cease and the cycle begun again.

Flow of current from the secondary battery will result in excessive evolution of hydrogen at the cathode, causing the metal plated to be highly porous. Since periods of deposition of soft porous metal alternate with periods of deposition of hard smooth metal, the resultant is a coating that is hard and adherent but highly porous, consisting of alternate layers of spongy and smooth metal. In this manner, the invention provides the high catalytic activity of porous plated metal with the tenacity and strength of smooth plated metal and the composition is suitable for commercial use.

According to the embodiment of Figure 2, currents of different potential are alternately applied between anode 20 and cathode 21 across a plating bath 22 from different sources by a mechanical timing device. The primary, low potential circuit includes battery 23 and variable resistance 25; while the secondary high potential circuit comprises battery 26 and variable resistance 27. The two circuits are connected in parallel across the plating bath through an ammeter 24 and a driven commutator 28. The commutator is adapted to alternately apply high and low potentials across the bath either by alternately closing the primary circuit and the secondary circuit or by maintaining the primary circuit closed while alternately opening and closing the secondary circuit.

The invention will be further understood from specific examples given below comparing catalysts prepared according to the invention with catalysts prepared by other methods of electroplating.

#### EXAMPLE I

A hard, shiny, non-porous nickel plate was produced on a steel screen by connecting the screen as cathode in a conventional plating setup, using an aqueous bath of pH 4 to 5 containing 0.30 N. NiSO<sub>4</sub>, 0.08 N. NH<sub>4</sub>Cl and 0.08 M. H<sub>3</sub>BO<sub>3</sub>. A current density of 1 ampere per square decimeter was applied and the bath vigorously agitated.

This plating was tested as a catalyst and was found to possess very little activity.

#### EXAMPLE II

A hard, shiny, somewhat porous nickel plate containing a very large number of tiny pinholes in its surface was obtained by using the following conditions:

pH=2.0-2.5  
c. d.=1.0 amp./dm.<sup>2</sup>  
Wt. deposit: 0.8 gram  
Time of plating: 3½ hours  
Solution concentrations:  
0.15 N. NiSO<sub>4</sub>  
0.04 N. NH<sub>4</sub>Cl  
0.04 M. H<sub>3</sub>BO<sub>3</sub>

The effect of this very acid solution was to produce a large number of very small hydrogen bubbles, which resulted in the "pinholed" type of plating. This plate was tested as a catalyst for the hydrogenation of C<sub>2</sub>H<sub>4</sub>, and was found to be a better catalyst than a shiny, smooth plate, but not as good as the porous plating of the preferred portion of this invention.

#### EXAMPLE III

A tough, porous, adherent nickel plate was formed by plating from a bath at a current density which produces a smooth plate, and simultaneously impressing sudden surges of exceedingly high voltage on the cell at short intervals of time. This may be accomplished by plating under the following conditions:

c. d.=1.5 amp./dm.<sup>2</sup>  
pH=4.6-5.5  
Agitation—slight  
Wt. plated metal: 0.35 gram  
Time of plating: 2½ hours  
Surges of overvoltage: 75 to 80 volts, intervals of 0.5-1 sec.  
Concentration of plating solution:  
0.30 N. NiSO<sub>4</sub>  
0.08 N. NH<sub>4</sub>Cl  
0.08 M. H<sub>3</sub>BO<sub>3</sub>

The overvoltage surges are obtained by a suitable timing arrangement. The positive pole of the high voltage source is connected to the positive pole of the plating cell. A diagram of the cell is shown in Figure 1. The effect of the surges of high voltage is to produce a very large number of tiny hydrogen bubbles which cause the plate deposited by the steady lower current to be porous. This plate was a very active catalyst for the reduction of C<sub>2</sub>H<sub>4</sub>.

#### EXAMPLE IV

Tough, porous, catalytically active plates may be obtained by plating from a solution containing a suspension of a precipitate, as for example, silica precipitate. Such a plate was obtained by using the following conditions:

pH=5.6-6.0  
c. d.=1.5 amp./dm.<sup>2</sup>  
Time of plating: 2½ hours  
Wt. of plate: 0.68 gram  
Agitation: Very vigorous  
Concentration of suspended SiO<sub>2</sub> ppt. 1%  
Concentration of plating solution:  
0.30 N NiSO<sub>4</sub>  
0.08 N. NH<sub>4</sub>Cl  
0.08 M. H<sub>3</sub>BO<sub>3</sub>

The silica gel was maintained in uniform suspension by vigorous stirring. It caused the hydrogen evolved on the cathode to be trapped on the surface and thus resulted in a porous plate.

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This plate was an excellent catalyst for the hydrogenation of  $C_2H_4$ .

## EXAMPLE V

A porous, tough, catalytically active nickel plated surface may be obtained by electrodepositing a heavy, smooth, uniform plate on an object, and then reversing the poles of the cell and plating part of this deposit off the object. This is accomplished by plating a smooth surface on the cathode by a known method. Then the plated cathode is placed in a bath at  $pH=1.0-2.0$ , and it is made the anode. Metal is removed partially at a current density of  $0.5-5.0$  amps. per  $dm.^2$ . It was found that almost any  $pH$  could be used with any current density, however, in practice, values are chosen which are most economical. The surface resulting from this treatment is very hard, porous, and adherent to the object on which plated. This plate was a very active catalyst for the reduction of  $C_2H_4$ .

## EXAMPLE VI

This example illustrates a method of regenerating the metallic catalysts of this invention when they have aged as a result of normal use in a catalytic process. The method of this example is applicable to the manufacture of new catalysts as it is obvious from the description below.

A porous nickel plated steel gauze which has been used as a hydrogenation catalyst and whose surface was partially sintered and catalytically inactive, was washed thoroughly with organic solvent to remove accumulated hydrocarbons, and ignited in air to remove carbon, and then reduced in  $H_2$  at  $500^\circ C$ . The catalyst is then plated in an electroplating cell, and made the anode.

$pH=1.5$

c. d. =  $3.0$  amps./ $dm.^2$

Concentration of solution:

$0.15$  N.  $NiSO_4$

$0.04$  N.  $NH_4Cl$

$0.04$  M.  $H_3BO_3$

As the current flows through cell, part of the spent plate is removed from the steel gauze, exposing fresh nickel surfaces. The catalyst is then made the cathode, the  $pH$  of the bath adjusted with aqueous ammonia, and a porous, adherent, catalytically active surface plated on at  $pH 5.0$ , and a current density of  $1.0-1.5$  amps./ $dm.^2$ . It is noted that catalyst regeneration by this method results in  $100\%$  recovery of the catalyst metal.

## EXAMPLE VII

A porous, adherent, catalytically active nickel plate may be produced by plating alternately at current densities which produce smooth and porous plates for short intervals of time, as  $5-20$  seconds. In this example the following conditions were used:

$pH=4.5-5.5$

c. d. alternately for 5 seconds:

$1.0$  amp./ $dm.^2$

$2.0$  amp./ $dm.^2$

Agitation: very slight

Concentration of solution:

$0.15$  N.  $NiSO_4$

$0.04$  N.  $NH_4Cl$

$0.04$  M.  $H_3BO_3$

A timing device was used to control the current density. Figure 2 is a diagram of this type of

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plating cell. The alternate smooth plating onto the porous layers leads to a very adherent but porous surface. This plate was found to be an excellent catalyst for the hydrogenation of  $C_2H_4$ .

The periods of plating under the different current densities need not be equal. Very good results were obtained when the ratio of smooth to porous plating times varied between  $1$  to  $1$  and  $1$  to  $4$ . For example, good, adherent catalytic plates were formed by plating at  $1$  amp./ $dm.^2$  for 5 seconds and at  $2$  amp./ $dm.^2$  for 5, 10, 15 or 20 seconds.

The catalytic properties of the catalysts prepared in the above examples were evaluated by testing their efficiency in hydrogenating ethylene. Equal volumes of hydrogen and  $C_2H_4$  were recycled over the catalysts at  $150^\circ$  to  $155^\circ C$ . and atmospheric pressure for 5 minutes, and then analyzed. Approximately the same weight of catalyst was used in each experiment. The relative efficiencies of the catalysts are shown in Table 1:

Table 1

Catalyst	Per Cent Ethylene Hydrogenated
Unplated Steel	0.0
Example I	1.2
Example II	47.0
Example III	95.0
Example IV	100.0
Example V	85.0
Example VI	90.0
Example VII	100.0

## EXAMPLE VIII

This example illustrates the fact that catalytically active and adherent cobalt surfaces may also be produced by the methods described in the above examples. An adherent, porous cobalt surface was produced by using the following conditions:

$pH=5.1-6.7$

c. d. =  $0.5-1.0$  amp./ $dm.^2$

Concentration of solution:

$0.15$  N.  $CoSO_4$

$0.04$  N.  $NH_4Cl$

$0.04$  M.  $H_3BO_3$

Catalytically active cobalt surfaces are useful in reactions such as the hydrogenation of carbon monoxide by the Fischer-Tropsch process. In such an exothermic process, they afford an excellent means of heat transfer and hence heat control.

In general, hydrogenation of carbonaceous substances may be conducted in the presence of nickel, cobalt and iron catalyst prepared according to the present invention.

We claim:

1. The process for producing a porous catalytic metallic body consisting of a plurality of alternate layers of dense and porous nickel, which consists in the electrodeposition of nickel by imposing a current having a density of approximately  $1.5$  amperes per square decimeter across the electrodes of an electrolytic cell containing an aqueous electrolytic bath of  $0.30$  N. nickel sulfate having a  $pH$  between about  $4.6$  and about  $5.5$ , maintained at substantially room temperature, to effect the deposition of a smooth, dense layer of nickel, simultaneously imposing from a high voltage source, the poles of which are connected to poles of like charge of said electrolytic cell, sud-

den surges of overvoltage of between about 75 and about 80 volts at intervals of between about 0.5 and about 1 second to produce during the imposition of said overvoltage the deposition of a porous nickel layer, thereby effecting, as a result of said surges of overvoltage upon the steady lower current, an alternate deposition of smooth and porous layers of metallic nickel to yield a resulting composition characterized by high structural strength.

2. The process for producing a porous catalytic metallic body consisting of a plurality of alternate layers of dense and porous nickel, which consists in the electrodeposition of nickel by imposing a current having a density of approximately 1.5 amperes per square decimeter across the electrodes of an electrolytic cell containing an aqueous electrolytic bath of nickel sulfate, boric acid, and ammonium chloride having a pH between about 4.6 and about 5.5 to effect deposition of a smooth, dense layer of nickel, simultaneously imposing from a high voltage source, the poles of which are connected to poles of like charge of said electrolytic cell, sudden surges of overvoltage of between about 75 and about 80 volts at intervals of between about 0.5 and about 1 second to produce during the imposition of said overvoltage the deposition of a porous nickel layer, thereby effecting, as a result of said surges

of overvoltage upon the steady lower current, an alternate deposition of smooth and porous layers of metallic nickel to yield a resulting composition characterized by high structural strength.

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